

Neutron Reflectometric Investigation of a Dendrimer/Nanoparticle Hybrid Film at Air/water Interface

K. MITAMURA,¹⁾ M. UJIHARA,¹⁾ N. TORIKAI,²⁾
and T. IMAE^{*,1),3)}

¹⁾Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan, ²⁾Neutron Science Laboratory (KENS), High Energy Accelerator Research Organization, Oho, Tsukuba 305-0801, Japan, and ³⁾Research Center for Materials Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan

Poly(amido amine) dendrimers with azacrown core and hexyl spacers (aza-C6-PAMAM dendrimer) are amphiphilic and flexible in structure.¹⁾ Amine-terminated aza-C6-PAMAM dendrimers were adsorbed on gold and 3-mercaptopropionic acid (MPA) self-assembled monolayer (SAM) substrates, and multilayers were constructed.²⁾ Langmuir films at air/water interface were fabricated from ester-terminated dendrimers.³⁾ Although silver nanoparticles in subphase were adsorbed on dendrimers with face-on conformation in Langmuir films, the adhesion was less and the adsorbed nanoparticles were disordered.

In the present work, ester-terminals of aza-C6-PAMAM dendrimer were replaced to octyl groups in order to intensify the amphiphilicity, and the dendrimer/nanoparticle hybrid films at air/water interface were investigated. Gold nanoparticles (Au-NP) were adsorbed on Langmuir films of dendrimers and displayed fractal-like network texture at low surface pressure. When the hybrid films were compressed, the morphology of nanoparticle aggregates was changed to monolayer, where nanoparticles were uniformly dispersed and partly ordered. The nanoparticles in the hexagonal lattice array are located on hydrophilic azacrown center in the ordered lattice arrangement of dendrimers in face-on conformation. Fourteen dendrimer molecules were adsorbed on a nanoparticle but the location of dendrimers on a nanoparticle was not elucidated.

The determination of dendrimer distribution on nanoparticle surface was carried out using neutron reflectometry. A chloroform solution of octyl-terminated aza-C6-PAMAM dendrimer was spread on an Au-NP suspension subphase. After 1 hr, the film was compressed until the surface pressure reached to 5 mN/m and neutron reflectivity was measured on an ARISA (Advanced Reflectometer for Interface and Surface Analysis) of High Energy

Accelerator Research Organization (KEK) in Tsukuba, Japan.

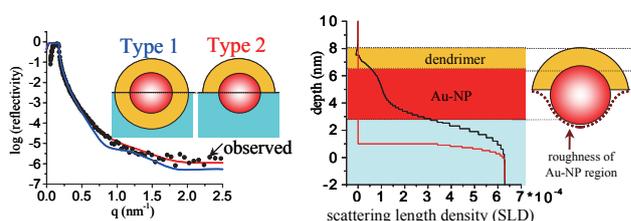


Fig.1 (Left) An observed neutron reflectivity curve of dendrimer/Au-NP hybrid Langmuir film and fitting curves based on Type 1 and 2 models, which were inset in figure. (Right) A depth vs. scattering length density profile of dendrimer/Au-NP hybrid Langmuir film (based on Type 2).

The observed neutron reflectivity curve in Fig. 1 displayed no characteristic fringes. Two types of models were applied for the simulation analysis using a theoretical equation. That is, (Type 1) dendrimers surround fully the surface of the Au-NP and (Type 2) dendrimers cover only the upper-half surface of Au-NP. From the comparison with observed one, it was indicated that only half of Au-NP surface is capped by dendrimers. The scattering length density-depth profile evaluated from best-fit parameters is shown in Figure 1. The calculated depths of Au-NP and dendrimer layers were reasonable in consistency with their evaluated sizes.

References

- 1) Yemul, O.; Ujihara, M.; Imae, T. *Trans. Mater. Res. Soc. Jpn.*, **2004**, *29*, 165.
- 2) Ujihara, M.; Imae, T. *J. Colloid Interface Sci.*, **2006**, *293*, 333.
- 3) Ujihara, M.; Orbulescu, J.; Imae, T.; Leblanc, R. M. *Langmuir*, **2005**, *21*, 6846.